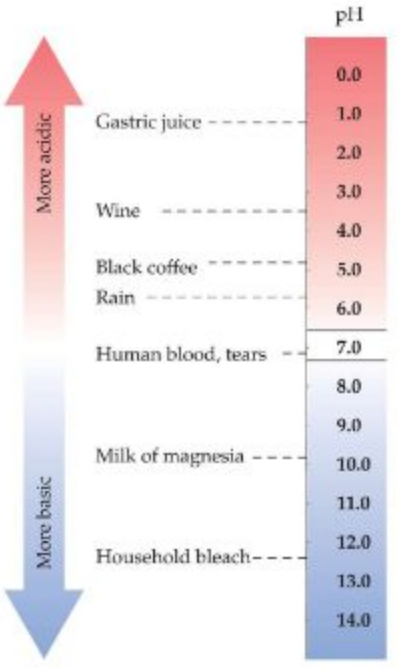
Chapter 16
Acid-Base Equilibria

Learning goals and key skills:

- Understand the nature of the hydrated proton, represented as either $H^+(aq)$ or $H_3O^+(aq)$
- Define and identify Arrhenuis acids and bases.
- Define and identify Bronsted-Lowry acids and bases, and identify conjugate acid-base pairs.
- Relate the strength of an acid to the strength of its conjugate base.
- Understand how the equilibrium position of a proton transfer reaction relates the strengths of acids and bases involved.
- Describe the autoionization of water and understand how $[H_3O^+]$ and $[OH^-]$ are related
- Calculate the pH of a solution given $[H_3O^+]$ or $[OH^-]$
- Calculate the pH of a strong acid or strong base given its concentration
- Calculate K_a or K_b for a weak acid or weak base given its concentration and the pH of the solution
- Calculate pH of a weak acid or weak base or its percent ionization given its concentration and K_a or K_b.
- Calculate K_b for a weak base given K_a of its conjugate acid, and similarly calculate K_a from K_b.
- Predict whether and aqueous solution of a salt will be acidic, basic, or neutral
- Predict the relative strength of a series of acids from their molecular structures
- Define and identify Lewis acids and bases.







Acids and Bases

Arrhenius

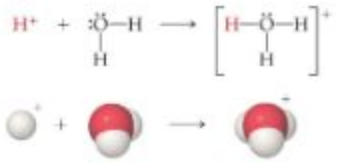
-An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions.

-A base is a substance that, when dissolved in water, increases the concentration of hydroxide ions.

Brønsted-Lowry

-An acid is a proton donor.

-A base is a proton acceptor.

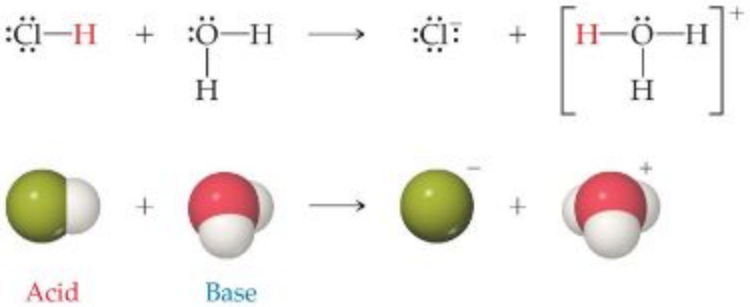


Acids and bases may be *inorganic* (7 strong acids, 8 strong bases) or *organic* (acids have –COOH group):

- HCl, HNO_3, H_2SO_4, HBr, HI, $HClO_3$, $HClO_4$
- AOH (A = Li, Na, K, Rb, Cs); $A(OH)_2$ (A = Ca, Sr, Ba)

What happens when an acid dissolves in water?

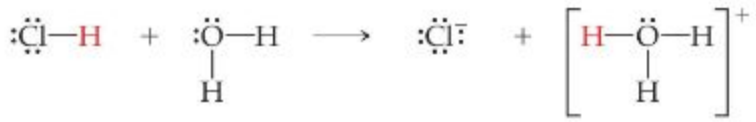
$$HCl(g) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq)$$



Acid Base

- Water acts as a Brønsted-Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the conjugate base of the acid and a hydronium ion are formed.

Amphiprotic – a substance that is capable of acting as an acid or a base e.g. H_2O, HCO_3^-, HSO_4^-.

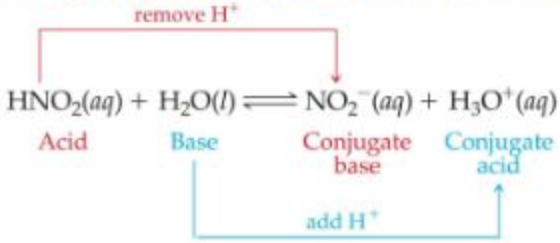


Acid Base

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Base Acid

Conjugate acids and bases



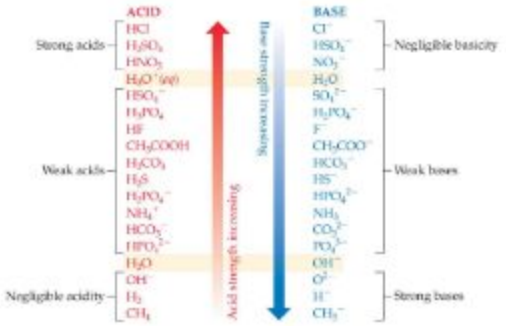
$HCN\ (aq) + H_2O\ (l) \rightleftharpoons CN^-\ (aq) + H_3O^+\ (aq)$

$HClO\ (aq) + H_2O\ (l) \rightleftharpoons ClO^-\ (aq) + H_3O^+\ (aq)$

$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-(aq)$

Acid and base strength

Strong acids are completely dissociated in water. Their conjugate bases are weak.

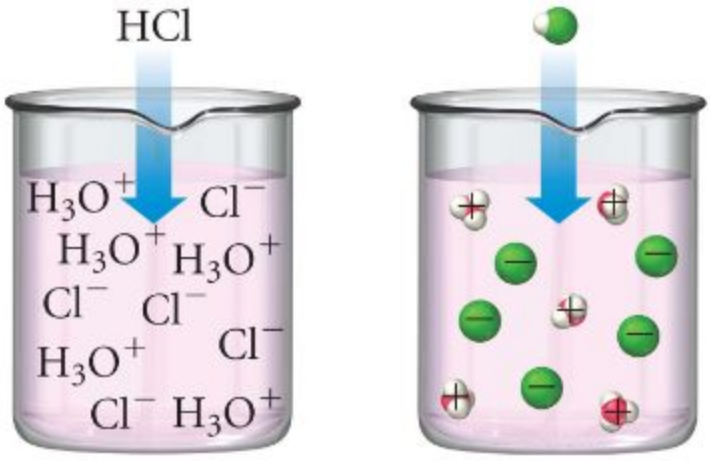


Weak acids only dissociate partially in water. Their conjugate bases are **strong**.

In any acid-base reaction, the equilibrium will favor the reaction that moves the proton to the stronger base.

A Strong acid

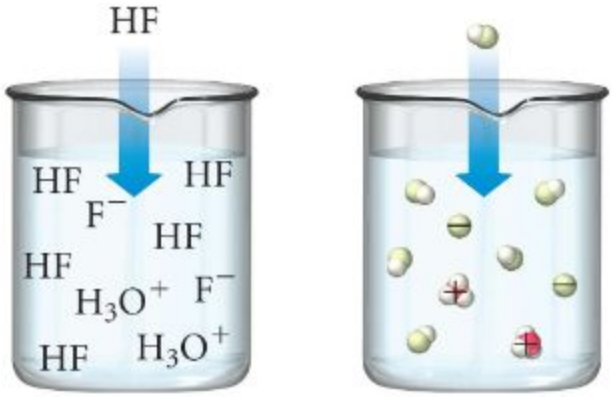
When HCl dissolves in water, it ionizes completely.



$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

A Weak acid

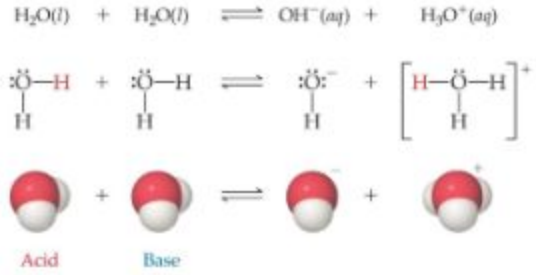
When HF dissolves in water, only a fraction of the molecules ionize.



$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

Autoionization of water

Water is amphoteric. In pure water, some molecules act as bases and some as acids. This is referred to as autoionization.



$K_w = [H_3O^+][OH^-]$

- This equilibrium constant is referred to as the ion-product constant for water, K_w.
- At 25°C, $K_w = 1.0 \times 10^{-14}$

Temperature dependence of K_w

Temperature	$K_w = [H_3O^+]\,[OH^-]$
0 °C	0.114×10^{-14}
25 °C	1.008×10^{-14}
50 °C	5.476×10^{-14}
75 °C	15.85×10^{-14}
100 °C	51.3×10^{-14}

Acidic, neutral, and basic solutions



Acidic solution
$[H^+] > [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

Neutral solution
$[H^+] = [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

Basic solution
$[H^+] < [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

neutral, $[H^+] = [OH^-]$
acidic solution, $[H^+] > [OH^-]$
basic solution, $[H^+] < [OH^-]$

pH and pOH scale

$pH = -\log [H_3O^+]$

$pOH = -\log [OH^-]$

- At 25 °C in pure water,

$$K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$$

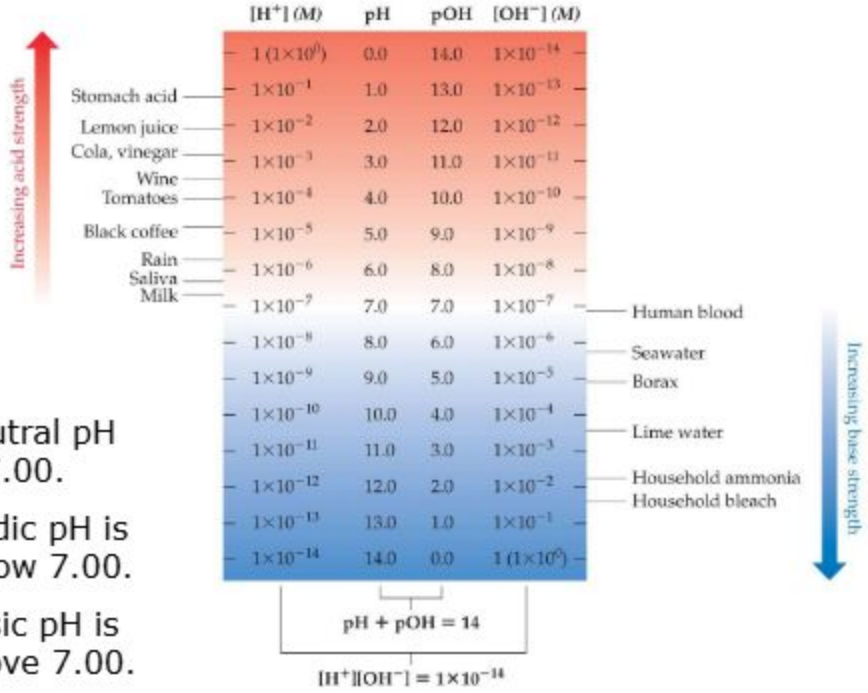
Since in pure water $[H_3O^+] = [OH^-]$,

$$[H_3O^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

$$pH + pOH = pK_w = 14.00$$

TABLE 16.1 Relationships between $[H^+]$, $[OH^-]$, and pH at 25 °C for Acidic, Neutral, and Basic Aqueous Solutions

	Acidic	Neutral	Basic
pH	<7.00	7.00	>7.00
$[H^+](M)$	$>1.0 \times 10^{-7}$	1.0×10^{-7}	$<1.0 \times 10^{-7}$
$[OH^-](M)$	$<1.0 \times 10^{-7}$	1.0×10^{-7}	$>1.0 \times 10^{-7}$



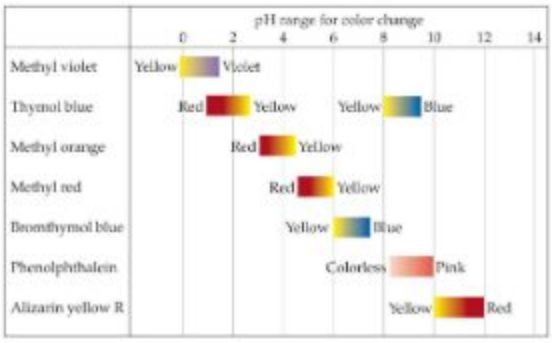
Neutral pH is 7.00.

Acidic pH is below 7.00.

Basic pH is above 7.00.

Three ways to measure pH

- Litmus paper
  red-to-blue:
  basic, pH > 8
  blue-to-red:
  acidic, pH < 5
- An indicator
- A pH meter

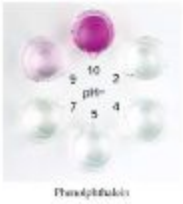












Strong acids completely ionize.

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

For the monoprotic strong acids,

$$[H_3O^+] = [\text{acid}]$$

- HCl, HNO_3, H_2SO_4, HBr, HI, $HClO_3$, $HClO_4$

Strong bases completely ionize.

$$MOH(aq) \rightarrow M^+(aq) + OH^-(aq) \quad \textit{or}$$

$$M(OH)_2(aq) \rightarrow M^{2+}(aq) + 2\ OH^-(aq)$$

- AOH (A = Li, Na, K, Rb, Cs); $A(OH)_2$ (A = Ca, Sr, Ba)

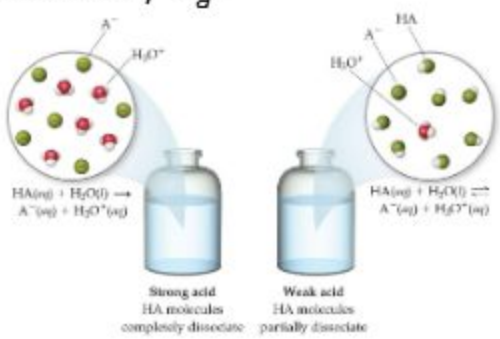
Weak Acids

- For a weak acid, the equation for its dissociation is

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

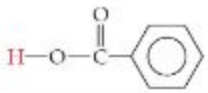
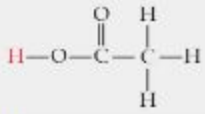
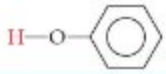
- Since it is an equilibrium, there is an equilibrium constant related to it, called the **acid-dissociation constant**, K_a:

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$



Dissociation Constants

TABLE 16.2 Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous ($HClO_2$)	H—O—Cl—O	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	H—F	F^-	6.8×10^{-4}
Nitrous (HNO_2)	H—O—N=O	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)		CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	H—O—Cl	OCl^-	3.0×10^{-8}
Hydrocyanic (HCN)	H—C≡N	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	1.3×10^{-10}

*The proton that ionizes is shown in red.

The greater the value of K_a, the stronger is the acid.

Calculating K_a from the pH

The pH of a 0.100 *M* solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

$$HCOOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HCOO^-\ (aq)$$

We know that $$K_a = \frac{[H_3O^+]\,[HCOO^-]}{[HCOOH]}$$

To calculate K_a, we need the equilibrium concentrations of all three things.

We can find $[H_3O^+]$, which is the same as $[HCOO^-]$, from the pH.

Calculating K_a from pH

Now we can set up an ICE table…

	[HCOOH], *M*	$[H_3O^+]$, *M*	$[HCOO^-]$, *M*
Initially	0.100	0	0
Change			
Equilibrium			

Calculating Percent Ionization

$$\text{Percent Ionization} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%$$

In this example,

$$\text{Percent Ionization} = \frac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100\%$$

$$[H_3O^+]_{eq} = 4.2 \times 10^{-3}\ \text{M}$$

$$[HCOOH]_{initial} = 0.10\ \text{M}$$

$$\text{Percent Ionization} = \frac{4.2 \times 10^{-3}}{0.10} \times 100\%$$

$$= 4.2\%$$

Method to Calculate pH Using K_a

1) Write the chemical equation for the ionization equilibrium.
2) Write the equilibrium constant expression.
3) Set up a table for Initial/Change in/Equilibrium Concentration to determine equilibrium concentrations as a function of change (x).
4) Substitute equilibrium concentrations into the equilibrium constant expression and solve for x. (Make assumptions if possible)

Calculating pH from K_a

Calculate the pH of a 0.30 M solution of acetic acid, $HC_2H_3O_2$, at 25°C.

$$HC_2H_3O_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-(aq)$$

K_a for acetic acid at 25°C is 1.8×10^{-5}.

$$K_a = \frac{[H_3O^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Calculating pH from K_a

We next set up an ICE table…

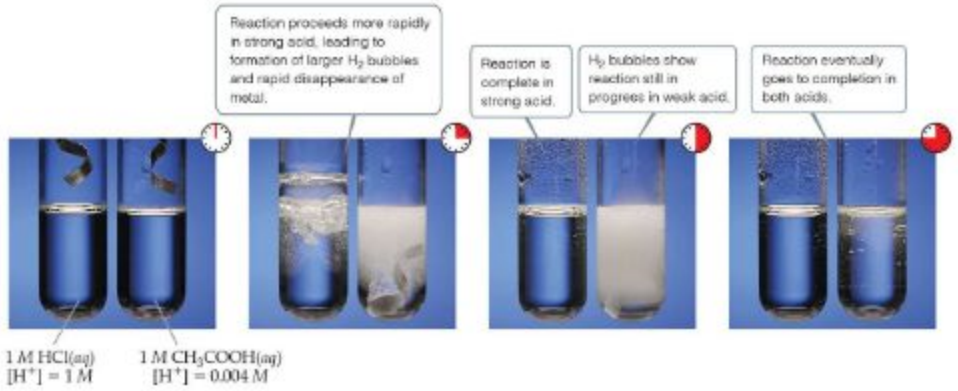
	$[HC_2H_3O_2]$, *M*	$[H_3O^+]$, *M*	$[C_2H_3O_2^-]$, *M*
Initially	0.30	≈0	0
Change			
Equilibrium			

We are assuming that x will be very small compared to 0.30 and can, therefore, be ignored.

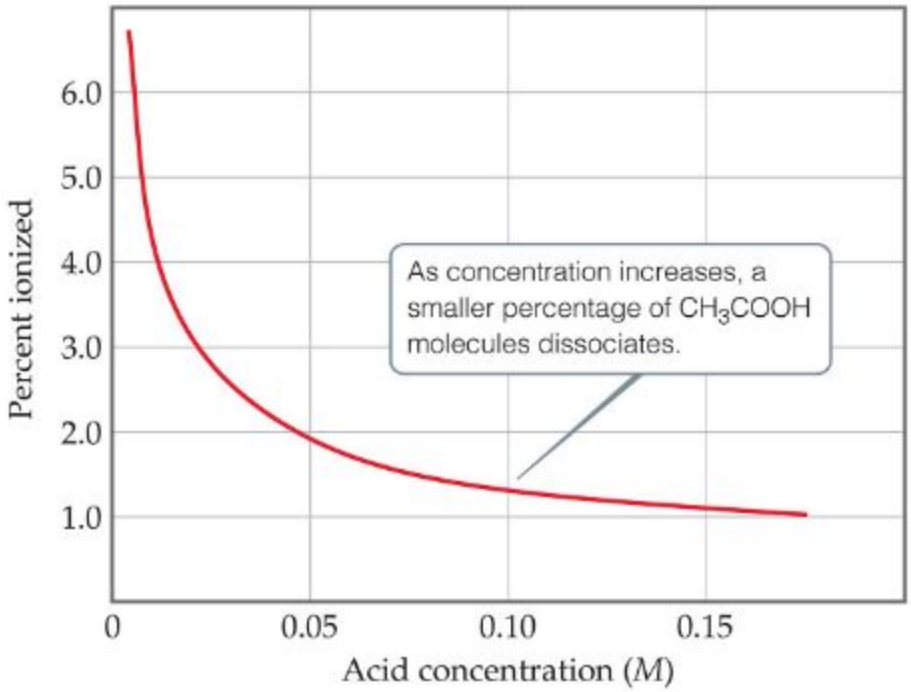
- $100*K_a = 100*(1.8 \times 10^{-5}) = 0.0018$
- $0.30\text{-}x = 0.30\text{-}0.0018 \approx 0.30$ (using sign. figures)

In general, the approximation that $[HA]_{eq}$ is effectively equal to $[HA]_0$ is valid whenever $[HA]_0$ is greater than $100*K_a$.

Strong vs. Weak Acids



Differences in conductivity and in rates of chemical reactions.



Polyprotic Acids…

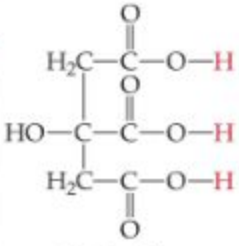
…have more than one acidic proton

Easier to remove the first proton than any successive proton.

If the difference between the K_a for the first dissociation and subsequent K_a values is 10^4 or more, the pH generally depends *only* on the first dissociation.

TABLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	HOOC—COOH	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$C_2H_2O_2(COOH)_2$	1.0×10^{-3}	4.6×10^{-5}	



Citric acid

Example (polyprotic acids)

$$H_3PO_4\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + H_2PO_4^-\,(aq)$$

$$K_{a1} = 7.5\times10^{-3}$$

$$H_2PO_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HPO_4^{2-}\,(aq)$$

$$K_{a2} = 6.2\times10^{-8}$$

$$HPO_4^{2-}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + PO_4^{3-}\,(aq)$$

$$K_{a3} = 3.6\times10^{-13}$$

Successive K_a values are smaller; it is less favorable to remove H^+ from an increasingly negatively charged ion.

Calculate the concentration of all species present at equilibrium in a 0.10 M oxalic acid solution at 25 °C.

$H_2C_2O_4(aq) \rightleftharpoons H_3O^+(aq) + HC_2O_4^-(aq)$

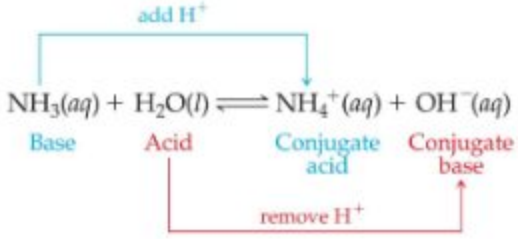
$K_{a1} = 6.5 \times 10^{-2}$

$HC_2O_4^-(aq) \rightleftharpoons H_3O^+(aq) + C_2O_4^{2-}(aq)$

$K_{a2} = 6.1 \times 10^{-5}$

Weak Bases

Bases react with water to produce hydroxide ion.



$$B\,(aq) + H_2O(l) \rightleftharpoons HB^+\,(aq) + OH^-\,(aq)$$

The equilibrium constant expression for this reaction is:

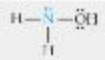
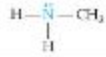
$$K_b = \frac{[HB^+]\,[OH^-]}{[B]}$$

where K_b is the base-dissociation constant.

Weak Bases

K_b can be used to find [OH^-] and, through it, pH.

TABLE 16.4 Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)		NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine ($HONH_2$)		$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)		$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	3.1×10^{-7}

*The atom that accepts the proton is shown in blue.

pH of Basic Solutions

What is the pH of a 0.15 *M* solution of NH_3 at 25 °C?

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Tabulate the data.

	[NH_3], *M*	[NH_4^+], *M*	[OH^-], *M*
Initial	0.15	0	0
Change			
Equilibrium			

Types of Weak Bases



Ammonia
NH_3

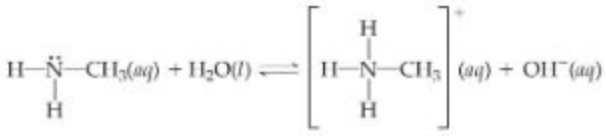
Two main categories

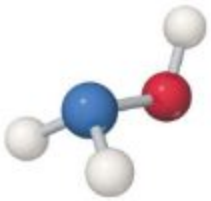
1) Neutral substances with an Atom that has a nonbonding pair of electrons that can accept H^+ (e.g. ammonia and the amines)



Methylamine
CH_3NH_2

2) Anions of weak acids





Hydroxylamine
NH_2OH

K_a and K_b

TABLE 16.5 Some Conjugate Acid–Base Pairs at 25 °C

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

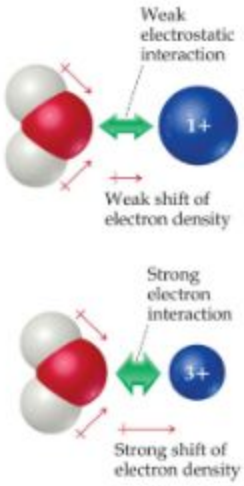
Therefore, if you know one of them, you can calculate the other.

Reactions of Anions with Water

- Anions are bases (conjugate base of an acid).
- As such, they can react with water in a hydrolysis reaction to form OH^- and the conjugate acid:

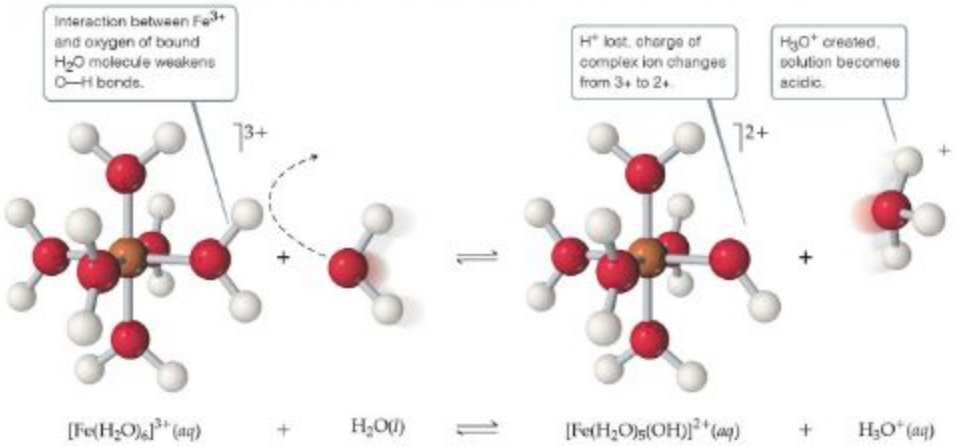
$$X^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HX_{(aq)} + OH^-_{(aq)}$$

Reactions of Cations with Water



- Cations with acidic protons (like NH_4^+) will lower the pH of a solution.
- Most metal cations that are hydrated in solution also lower the pH of the solution.

Reactions of Cations with Water



- Attraction between nonbonding electrons on oxygen and the metal causes a shift of the electron density in water.
- This makes the O-H bond more polar and the water more acidic.
- Greater charge and smaller size make a cation more acidic.

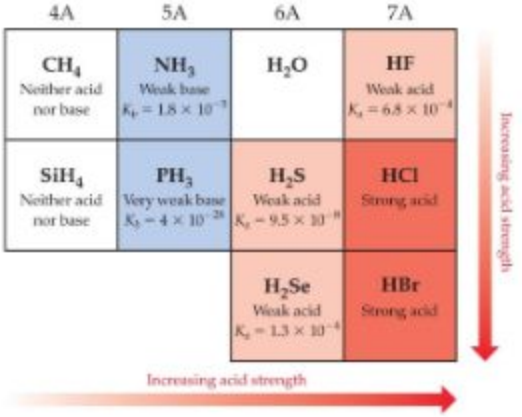
Effect of Cations and Anions

1. An anion that is the conjugate base of a strong acid will not affect the pH.
2. An anion that is the conjugate base of a weak acid will increase the pH.
3. A cation that is the conjugate acid of a weak base will decrease the pH.
4. Cations of the strong Arrhenius bases will not affect the pH.
5. Other metal ions will cause a decrease in pH.
6. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the K_a and K_b values.



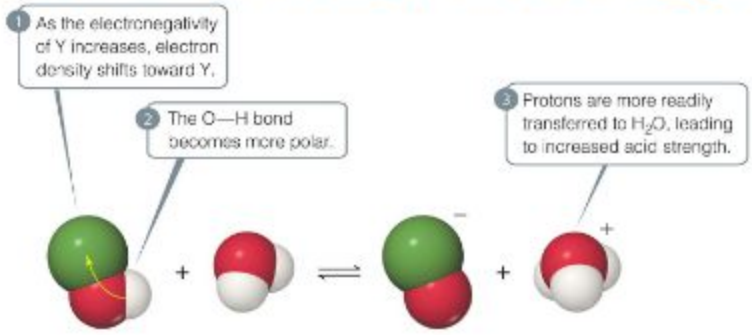


Factors Affecting Acid Strength



- The more polar the H-X bond and/or the weaker the H-X bond strength, the more acidic the compound.
- Acidity increases from left to right across a row and from top to bottom down a group.

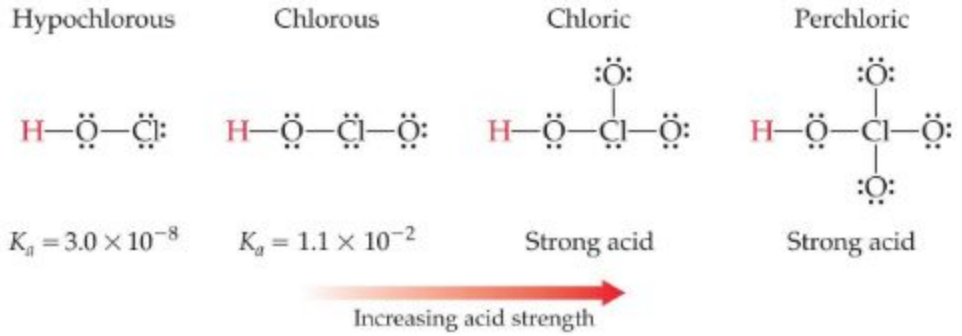
Factors Affecting Acid Strength



Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

In oxyacids, in which an -OH is bonded to another atom, *Y*, the more electronegative *Y* is, the more acidic the acid.

Factors Affecting Acid Strength



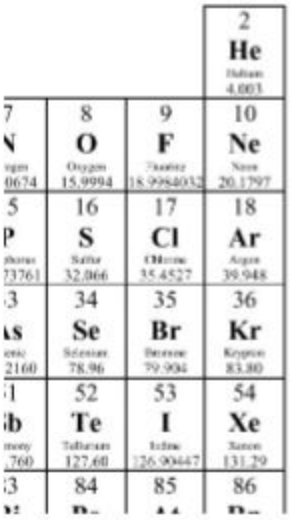
For a series of oxyacids, acidity increases with the number of oxygens.

- Strength of an acid increases as additional electronegative atoms are added

Arrange the following oxoacids in order of decreasing acid strength:

$HClO$, $HClO_2$, $HClO_3$, $HBrO$

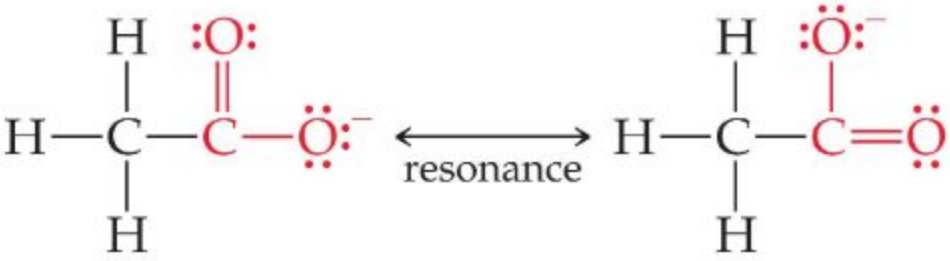
(rank strongest to weakest)



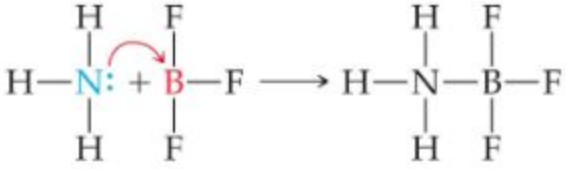
Factors Affecting Acid Strength

Acidic behavior of carboxylic acids

- The additional oxygen attached to carbon draws electron density from the O-H bond, increasing polarity and stabilizing the conjugate base anion.
- Resonance in the conjugate bases of carboxylic acids stabilizes the anion by spreading the negative charge over several atoms.



Lewis Acids and Bases



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted-Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.

Hydrated cations

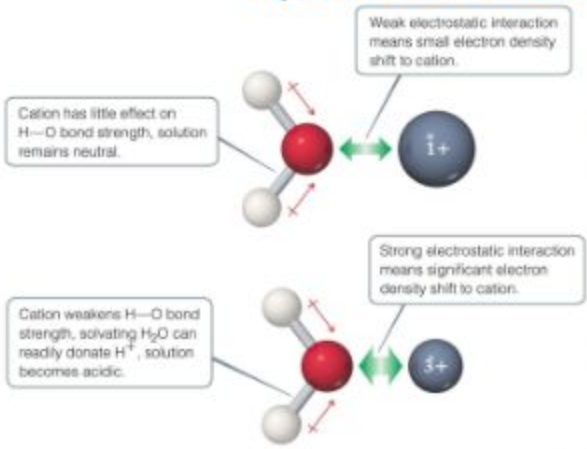


TABLE 16.6 Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

Cation	K_a
Fe^{3+}	6.3×10^{-3}
Cr^{3+}	1.6×10^{-4}
Al^{3+}	1.4×10^{-5}
Fe^{2+}	3.2×10^{-10}
Zn^{2+}	2.5×10^{-10}
Ni^{2+}	2.5×10^{-11}

$$M(H_2O)_6^{n+}(aq) \rightleftharpoons M(H_2O)_5(OH)^{(n-1)+}(aq) + H^+(aq)$$

K_a values vary depending on the metal, meaning $[H^+]$ varies, thus pH depends on the metal.

$$K_a = \frac{[M(H_2O)_5(OH)^{(n-1)+}][H^+]}{[M(H_2O)_6^{n+}]}$$